 # 1. (10 points) Short Answer Questions * indicates partial points possible *

a) What is the half-life of a first order reaction with a rate constant of $1.43 * 10^{-3}$: (1)* (0.5 no units)

ln(2)/k = 485 s

b) According to the molecular collision theory, what are the two requirements for a bimolecular reaction to occur? (2)

1. **Enough kinetic energy to overcome the E_a**
2. **Correct orientation (geometry)**

c) What is the value of K_b associated with the reaction below: (1) $K_b = K_w/K_a = 5.3 \times 10^{-10}$

$$N_3^- + H_2O \rightleftharpoons HN_3 + OH^-$$

d) The conjugate acid and conjugate base of $H_2PO_4^-$ are ___ H_3PO_4__ and ___ HPO_4^{2-}____, respectively. (2)*

e) Using the following information: (1)*

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad K_c = 1.13 * 10^{-2}$$

$K_2 = (K_c)^4 = 1.63 \times 10^{-8}$

$$P_4(s) + 6Cl_2(g) \rightleftharpoons 4PCl_3(g) \qquad K_c = 2.00 * 10^{-19}$$

$K_1 = 1/K_c = 5.00 \times 10^{18}$

Determine K_c for: $4\,PCl_5(g) \rightleftharpoons P_4(s) + 10\,Cl_2(g)$

$K_c = K_1 \times K_2 = 8.15 \times 10^{10}$

f) Show the full ionic equation and the net ionic equation associated with the reaction of Na_2SO_4(*aq*) with $Ba(NO_3)_2$(*aq*).

Ionic equation: (1)*

$2\,Na^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2\,NO_3^-(aq) \rightarrow BaSO_4(s) + 2\,Na^+(aq) + 2\,NO_3^-(aq)$

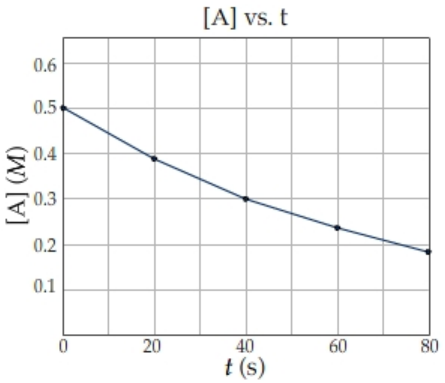
Net Ionic equation: (1)* (Partial points only if aqueous phases are missing)

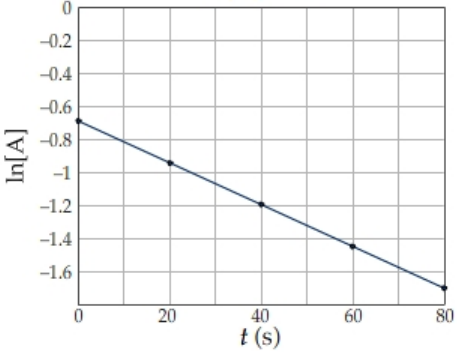
$SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$

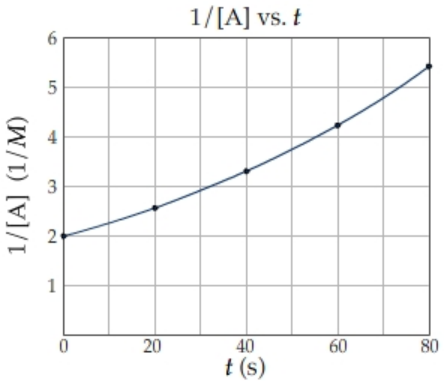
g) Which of the following compound(s) is(are) categorized as soluble: (1)*

$PbSO_4$ Ag_2S [✓ KOH] [✓ $MgSO_4$]

 # 2. (10 points) In a process described by the overall reaction $2\text{A} \longrightarrow \text{B}$, the following graphs can be obtained from experimental data, all at 295 K:







a) What is the order for the reaction? (*circle one answer*) **(1)**

Zero order [✓ **First order**] **Second order** **Third order**

b) What is the value of the rate constant for the reaction? (3) (1 calc / 1 answer / 1 units)

k = -slope = $-\left(\frac{\Delta \ln[A]}{\Delta t}\right) = -\left(\frac{\ln[A]_f - \ln[A]_i}{t_f - t_f}\right) = -\left(\frac{-1.7-(-0.7)}{80s - 0s}\right) = 1.25\text{x}10^{-2}$

Answer: 1.25 x 10^{-2} s^{-1}

d) Using the appropriate integrated rate law, determine the expected concentration of A at 90 seconds. (3)

$$\ln[A]_t = -kt + \ln[A]_o \qquad \ln[\text{A}]_{90s} = -1.25\text{x}10^{-2}s^{-1} \bullet 90s + \ln[0.5\text{M}]$$

$$\ln[\text{A}]_{90s} = -1.81$$

$$[\text{A}]_{52s} = e^{\ln[A]} = e^{-1.81} = 0.162\text{M}$$

Answer: 0.162M

d) Knowing that the rate constant (k) is 0.0357 s^{-1} for the same reaction at 325 K, calculate the activation energy of the reaction. (3)

$$\ln\left(\frac{k_2}{k_1}\right) = \left(-\frac{\text{Ea}}{\text{R}}\right)\left(\frac{1}{\text{T}_2} - \frac{1}{\text{T}_1}\right) \qquad \ln\left(\frac{3.57\text{x}10^{-2}}{1.25\text{x}10^{-2}}\right) = \left(-\frac{\text{Ea}}{8.31451\ \text{JK}^{-1}\text{mol}^{-1}}\right)\left(\frac{1}{325} - \frac{1}{295}\right)$$

$$\text{Ea} = \ln\left(\frac{3.57\text{x}10^{-2}}{1.25\text{x}10^{-2}}\right) \bullet \frac{1}{\left(\frac{1}{325\text{K}} - \frac{1}{295\text{K}}\right)} \bullet -8.31451\ \text{JK}^{-1}\text{mol}^{-1} = 27886\ \text{J/mol} = 27.9\ \text{kJ/mol}$$

Answer: 27.9 kJ/mol

 # 3. (10 points) The production of sulfuric acid involves as one of its step the oxidation of sulfur dioxide with excess oxygen to produce sulfur trioxide, according to the following equilibrium:

$$2\ \mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\ \mathrm{SO_3}(g) \qquad \Delta\mathrm{H} = -\ 197\ \mathrm{kJ/mol}$$

a) In a reaction, 1.18 mol of SO_2, 0.700 mol of O_2 and 0.526 mol of SO_3 are introduced simultaneously in a 2.00 L vessel at 1000 K. Once equilibrium is reached, 0.240 mol of O_2 remain in the vessel. Determine the equilibrium amount of SO_2 and SO_3 (in mol), as well as the equilibrium constant K_c for the reaction. **(6)**

Initial concentrations: 0.590 M SO_2, 0.350 M O_2, 0.263 M SO_3

Final concentrations: 0.120 M O_2

	$2\ SO_2(g)$ +	**$O_2\ (g)$** $\rightleftharpoons$	**$2\ SO_3(g)$**
I *(1 pt)*	0.590	0.350	0.426
C *(1 pt)*	**- 0.460**	**- 0.230**	**+ 0.460**
E *(1 pt)*	**0.130**	0.120	**0.723**

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 \bullet [O_2]} = \frac{0.723^2}{0.130^2 \bullet 0.120} = 258$$

(1 pt – formula, 1 pt concentration & answer)

Equilibrium SO_2: **0.260 mol *(0.5pt)*** **Equilibrium SO_3:** **1.45 mol *(0.5pt)*** **K_c: 258**

b) Determine the value of K_p at 1000 K (work with pressure units in atmospheres: i.e. *atm*). **(2)**

$$K_p = K_c \bullet (RT)^{\Delta n} = 258 \bullet (0.08206\ \ \mathrm{atm \cdot L \cdot K\text{-}1 \cdot mol\text{-}1\ x\ 1000K})^{2-3}$$
$$K_p = 3.14$$

K_p: 3.14

c) From the equilibrated mixture obtained in a), would a reduction of the vessel volume from 2L to 1L shift the equilibrium towards the products, the reactants or not affect the equilibrium at all? Provide brief reasoning for your answer.

A shift of the equilibrium towards the products is expected, to reduce the overall number of moles (2 for the products instead of 3 for the reactants) .

 # 4. (10 points) Fractional separation involves precipitating one ion voluntarily while keeping the other in solution. In an attempt to separate chloride and iodide ions, an aqueous solution of 2.00 M $AgNO_3$ is slowly added to a solution of 0.0170 M in Cl^- and 0.300 M in I^-.

a) Which anion, between Cl^- and I^-, precipitates first? (*You need to show your work*) **(5)**

Calculate the $[Ag^+]$ at which both ions would start precipitate from K_{sp} values:

For chlorine: (2)

$K_{sp} = [Ag^+][Cl^-]$ hence: $[Ag^+] = K_{sp} / [Cl^-] = 1.8 \times 10^{-10} / 0.0170\ M = 1.1 \times 10^{-8}\ M$

For Iodine: (2)

$K_{sp} = [Ag^+][I^-]$ hence: $[Ag^+] = K_{sp} / [I^-] = 1.5 \times 10^{-16} / 0.300\ M = 5.0 \times 10^{-16}\ M$

Once the concentration of Ag^+ reaches 5.0×10^{-16} M (the smaller of the two conc.), AgI will start to precipitate (1)

Answer: I^- precipitates (as AgI) first.

b) When the second anion (Cl^- or I^-) starts to precipitate, what is the remaining concentration of the first anion in solution. (4)

When AgCl starts to precipitate, the concentration of Ag+ will be 1.2×10^{-8} M (found in part a – *1 pt*). At this point, concentration of I^- can be found from Ksp.

$K_{sp} = [Ag^+][I^-]$

hence: $[I^-] = K_{sp} / [Ag^+] = 1.5 \times 10^{-16} / 1.1 \times 10^{-8}\ M = 1.36 \times 10^{-8}\ M$ (*1 pt formula, 1 pt answer*)

Answer: 1.36×10^{-8} M (*units 1 pt*)

c) Assume that the separation of ions is effective if > 99 % of the first ions have precipitated while the other type is still in solution. **Would you consider this system appropriate for the separation of Cl^- from I^-?** (*Circle one answer*) **(1 – has to match answer in b)**

[✓ YES] **NO**

 # 5. (10 points) A student prepares a 0.250 M solution of an unknown monoprotic acid (HA). At equilibrium, he measures a pH for the solution of 4.45. **(6)**

a) What is the acid dissociation constant (K_a) for the acid?

At equilibrium: pH = - log [H+] = 4.45

[H+] = 10^{-pH} = $10^{-4.45}$ = 3.54 x 10^{-5} (1 pt formula, 1 pt answer)

1 pt overall	**HA $\rightleftharpoons$**	**H+ +**	**A-**
I	0.250	0	0
C ***(1 pt stoichiometry)***	**-3.54 x 10^{-5}**	**+3.54 x 10^{-5}**	**+3.54 x 10^{-5}**
E	**~0.250**	**3.54 x 10^{-5}**	**3.54 x 10^{-5}**

$$\boxed{K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[3.54 \text{ x } 10^{-5}]^2}{0.250} = 5.01 \text{ x } 10^{-9}}$$ **(1 pt formula, 1 pt answer)**

Answer: **5.01 x 10^{-9}**

b) A lab technician is trying to determine the concentration of his solution of cinnamic acid ($C_9H_7O_2H$ – MM 148 g/mol), a *monoprotic acid* commonly used in the manufacture of flavors and perfumes. **A 10.00 mL sample of the cinnamic acid solution is titrated to completion with 32.50 mL of 0.1250 M NaOH. What is the % mass of Cinnamic acid in the original solution (assume a density of 1.020 g/ml for the solution)? (4)**

(2 pts for the dimensional analysis / finding the grams of acid)

(1 pt for the % mass formula, 1 pt for final answer)

$$\text{g of acid} = 32.50 \text{ mL NaOH} \bullet \frac{1\text{L}}{1000\text{ml}} \bullet \frac{0.1250\text{mol NaOH}}{\text{L NaOH}} \bullet \frac{1 \text{ mol acid}}{1 \text{ mol NaOH}} \bullet \frac{148\text{g acid}}{1 \text{ mol acid}}$$

$$\text{g of acid} = 0.601\text{g}$$

$$\% \text{ mass acid} = \frac{0.601\text{g acid}}{10.00\text{mL}} \bullet \frac{1\text{mL}}{1.02\text{g}} * 100\% = 5.89\ \%$$

Answer: **5.89 %**